

SOLVATION EFFECTS AND GURNEY COSPHERE OVERLAPS: A CONDUCTIMETRIC APPROACH

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Abstract - It is shown that theoretical derivations of excess thermodynamic functions and of transport coefficients may be carried out in a self-consistent way. Examples are given for mean activity and conductance coefficients of dilute solutions of binary symmetrical electrolytes. This allows experimental data to be reduced in terms of parameters characterizing the specific short range interactions in solutions between anions and cations. These parameters represent the energy involved when the solvation cospheres of anions and cations overlap. Whenever possible check is made through experimental data processing that both techniques lead to the same quantitative results. An extensive set of results is presented for 1-1 salts in water and alcohols.

INTRODUCTION

Both excess thermodynamic data and conductance coefficients are functions of the ionic concentration in solutions. This concentration dependence varies from one electrolyte to another and thus is a function of the different ion-ion interactions so that the experimental data may be expected to be a source of information concerning these interactions and the influence of the solvent on these interactions. Indeed since the Debye-Hückel (DH) theory (Ref. 1) was issued many attempts were made in order to explain the values derived for the distance of closest approach which controls the DH theory in terms of solvent effects such as solvation numbers (Ref.2) for instance. The same was true for conductance which is often analyzed in terms of association constants without giving to this concept a clear definition though. As a result there remains in the mind of the non-specialist a feeling of confusion still enhanced by the fact that this field is very active not only on the experimental but also theoretical point of view. Each new derivation brings of course a contribution of its own which is not always clearly underlined, emphasis being made more on apparent contradictions with the former derivations which may seem to be irreducible.

The purpose of the authors would be reached if the readers could be convinced that both excess thermodynamic quantities and transport coefficients can indeed be treated in a classical and self-consistent way as initiated by Debye (Ref.1) and by Onsager (Ref.3); that the so-called "association" concept due to Bjerrum (Ref.4) can be extracted from the fundamental bases of this approach without any a-priori "chemical" assumption and that ultimately the same kind of information can be obtained from analysis of experimental data with the same reliability that is reached from modern and much more difficult treatments using purely numerical analysis. This information mainly concerns the specific energy involved when the solvation cospheres of the ions overlap. If lithium chloride and cesium iodide differ concerning the concentration dependence of their activity and conductance coefficients in solutions it is partly due to the fact the ionic components have not the same dimensions. However, it is well known now that these excluded volume effects are not sufficient to explain these differences. More important is the fact that around each ionic species the solvent molecules present different organizations. This is what is generally denoted as the Gurney cospheres. What really makes the specificity of each electrolyte is the so-far quantitatively unpredictable energy which is involved when these cospheres overlap i.e. when close ionic configurations statistically occur. There lies the reason why lithium chloride behaves as if it was composed of much larger ions than cesium iodide. In fact one knows that the cesium and iodide ions do not shrink at washing to use Stoke's striking image (Ref.5), but rather that solvation effects in water are such that short range cesium-iodide ionic configurations are favoured and that the opposite occurs for lithium chloride. The purpose of this study is to measure these effects quantitatively through use of the conductance technique following the road opened by Rasaiah and Friedman who used excess thermodynamic data.

THE CASE OF EQUILIBRIUM

For dilute electrolyte solutions ($c < 0.1$ M) where the McMillan-Mayer scale practically coincides with the Lewis-Randall scale (Ref.6), the compressibility equation (Ref.7) tells us that from thermodynamical excess data, we can only expect informations concerning the zeroth moments G_{ij} of the solute-solute distribution functions g_{ij}

$$G_{ij} = \int 4\pi r^2 (g_{ij}(r)-1) dr \quad (1)$$

This is clearly shown by the compressibility equation which in the special case of a symmetrical electrolyte solution reads

$$\frac{d \ln f_{\pm}}{dc} = - \frac{G_{+-} + \frac{1}{2}(G_{++} + G_{--})}{1 + c[G_{+-} + \frac{1}{2}(G_{++} + G_{--})]} \quad (2)$$

where f_{\pm} is the mean activity coefficient of the electrolyte. This relation tells that in dilute solution one can only expect to obtain quantitative information not on the direct energy of interactions U_{ij} themselves but rather on average value of the exponential of these quantities, mainly

$$\int_0^R r^2 \exp\left(-\frac{U_{ij}}{kT}\right) dr.$$

This may seem a disappointingly restrictive fact but it is not surprising though. It is indeed too ambitious a goal to expect more detailed information on the U_{ij} functions from the observed deviations from the limiting laws for excess quantities.

From eq.(2) the following result can be obtained (Ref.8)

$$\left\{ \begin{array}{l} \ln f_{\pm} = \ln f_{\pm}^L(R,c) + \ln \gamma + O(c) \\ \frac{1-\gamma}{\gamma} = c G_{+-}^S \end{array} \right. \quad (3)$$

$$\quad (4)$$

after splitting the integrals of the type of eq.(1) into short range

$$G_{ij}^S = \int_0^R 4\pi r^2 (g_{ij}(r)-1) dr \quad (5)$$

and long range contributions

$$G_{ij}^L = \int_R^{\infty} 4\pi r^2 (g_{ij}(r)-1) dr \quad (6)$$

where R is completely arbitrary so far. The quantity f_{\pm}^L is a long range activity coefficient obtained from eq.(2) in which only the G_{ij}^L are used. The dimensionless quantity γ is defined by

$$\gamma = \frac{1}{1+cG_{+-}^S} \quad (7)$$

Obviously it follows the relation

$$0 \leq \gamma \leq 1 \quad (8)$$

Finally the $O(c)$ function in eq.(3) contains all neglected terms in the derivation of the system of eqs.(3,4) from eq.(2) that is:

- all terms deriving from short range anion-anion and cation-cation interactions through G_{+-}^S (and G_{--}^S);
- also terms in $O(c^{3/2})$ issued from cross products such as G_{ij}^L , G_{kl}^S and
- finally, terms in $O(c^{3/2})$ issued from the last integral in the expression

$$-\int \frac{G_{+-}^S}{1+cG_{+-}^S} dc = \ln \frac{1}{1+cG_{+-}^S} - \int^c \frac{dG_{+-}^S}{1+cG_{+-}^S} dc \quad (9)$$

which is not explicitly considered in eqs.(3,4).

The analogy between the system of eqs.(3,4) and the Bjerrum equations

$$\left\{ \begin{array}{l} \ln f_{\pm} = - \frac{kq\gamma^{1/2}}{1+kR\gamma^{1/2}} + \ln \gamma \\ \frac{1-\gamma}{\gamma c f_{\pm}^L} = K_A = \int_0^R 4\pi r^2 \exp\left(-\frac{U_{+-}(r)}{kT}\right) dr \end{array} \right. \quad (10)$$

$$\quad (11)$$

is obvious, where U_{+-} is any direct anion-cation pair potential. More details concerning this point will be found in the original publications. Let us just recall that Bjerrum result is equivalent to proposing the Debye-Hückel approximation for $f_{\pm}^L(R,C,\gamma)$ in eq.(3) and consequently the choice for R is then no longer arbitrary and it was found (cf.Ref.16) that

$$R = q = \frac{(z_1 z_2) e^2}{2DkT} \quad (12)$$

was very reasonable. Also Bjerrum considered only the primitive model so that the Bjerrum "association constant" in eq.(11) reduced to

$$K_A^B = \int_a^q 4\pi r^2 \exp\left(\frac{2q}{r}\right) dr \quad (13)$$

where a is the distance of closest approach of the hard sphere anion and cation. Another important step is the identification of eqs(4) and (11) which implies

$$G_{+-}^S = \gamma_{\pm}^2 L^2(R, c) K_A \quad (14)$$

This may be achieved (Ref.9) by choosing a good approximation for the distribution function $g_{+-}(r)$ in eq.(5) in the short range region $0 < r < R$.

One first trial is to use the Meeron distribution function

$$g_{+-}(r) = \exp\left(-\frac{U_{+-}^*}{kT} + \frac{2q}{r} e^{-\kappa r}\right) \quad (15)$$

where U_{+-}^* is the short range part of the direct interaction energy. For the primitive model

$$U_{+-}^* = \infty \text{ if } r < a. \quad (16)$$

For other hamiltonian models specific interaction parameters may be further introduced such as Rasaiah-Friedman square mound perturbation (Refs.10&11). Expanding the Debye screening factor $e^{-\kappa r}$ in the short range region and truncating after the second term

$$e^{-\kappa r} \approx 1 - \kappa r \quad (17)$$

leads ultimately to the following result

$$G_{+-}^S \approx f_{\pm LL}^2 K_A \quad (18)$$

where $f_{\pm LL}$ is the Debye-Hückel limiting law,

$$f_{\pm LL} = \exp(-\kappa q). \quad (19)$$

Obviously eq.(18) is a first approximation to the probably more exact result given by eq.(14). This means that the Meeron distribution function (15) is still too crude an approximation itself to represent the anion-cation distribution function. It can be shown that the Meeron distribution function can be obtained from the Poisson-Boltzmann equation

$$\Delta\psi_i = \frac{\kappa^2 e_i}{2qD} \text{ sh } \frac{e_i \psi_i}{kT} \quad (20)$$

where ψ_i is the mean electrical potential at a point of the atmosphere of the reference ion of charge e_i ; D the dielectric constant of the medium; T is the Kelvin temperature and k the Boltzmann constant. Linearizing eq.(20) leads directly to the Debye starting equation

$$\Delta\psi_i = \kappa^2 \psi_i. \quad (21)$$

A less crude approximation was used by Fuoss and Onsager (Refs.13&14) in the short range region: it consists in substituting the mean potential ψ_i in the RHS of eq.(21) by the direct potential and approximating $\text{sh}(\chi \gg 0)$ by $\exp(\chi)/2$. It comes

$$\Delta\psi_i \approx \frac{\kappa^2 e_i}{2qD} \exp\left(\frac{2q}{r}\right) / 2. \quad (22)$$

Inspection of the Fuoss-Onsager result which we shall denote $\psi_i^{(1)}$ shows that it leads to a first approximation for G_{+-}^S which we shall write

$$G_{+-}^S(1) = f_{\pm}^2 K_A, \quad (23)$$

a result which is similar to the former result given by eq.(18) which was obtained from the Meeron distribution function. However, it is now possible to carry the Fuoss-Onsager calculation further by an iterative process which consists in substituting $\psi_i^{(1)}$ to the exponential argument in eq.(22). The result for G_{+-}^S reads then

$$G_{+-}^S(2) = f_{\pm}^2 K_A (1 - K_A c). \quad (24)$$

One sees that the iterative procedure can be carried out indefinitely and that the final

result will read

$$\begin{aligned} G_{+-}^S(n) &= f_{\pm}^2 K_A (1 - K_A c (1 - K_A c (\dots) \\ &= \gamma' f_{\pm}^2 K_A \quad \text{when } n \rightarrow \infty \end{aligned} \quad (25)$$

with

$$\gamma' = \frac{1}{1 + K_A c} \quad (26)$$

Obviously γ' in eq.(26) and γ in eq.(7) coincide at lower concentrations so that eq.(4) then identifies whith Bjerrum's eq.(11) as expected.

It can be shown the concentration range of application of the Bjerrum set of eq.(10,11) is limited to

$$\kappa q \gamma^{1/2} < 0.5$$

approximately, where κ^{-1} is the Debye radius. Beyond that range, higher order short range clusters such as triplets for instance or anion-anion or cation-cation pairs which are not taken into account do lead to no longer negligible contributions. This is indeed a drastic restriction to the use of eqs.(10,11) since except for a few cases in aqueous solutions, thermodynamic excess quantity cannot be measured with sufficient precision in such a dilute range. Moreover, in water the Bjerrum equation is no drastic improvement over the original Debye-Hückel equation; one sees for instance that when the value of q approaches that of \underline{a} then the Bjerrum set reduces to the D-H equation

$$\ln f_{\pm} = - \frac{\kappa q}{1 + \kappa a} \quad (27)$$

This explains that for a long time the Bjerrum expression was not considered whith enough attention since it could hardly be significantly tested. In opposition its empirical character was severely judged mostly, at a time where its fundamental basis was overlooked. Using the clear and significant vocabulary introduced by Friedman (Ref.15) one can state that though it was introduced originally as a "chemical model" correction to an "equation model" derivation (that of Debye and Hückel), the sound bases of the Bjerrum formulation are now proved since it can be derived from an "hamiltonian model" calculation after a series of well controlled approximations.

These results must be considered as the generalization toward the complete Bjerrum formulation of a former analytical expression (Ref.16)

$$\ln f_{\pm} = -\kappa q + \kappa q \kappa R \left[1 - \delta \left(\frac{q}{R} \right) + \delta' \left(\frac{q}{R} \right) \right] - K_A c - \frac{1}{2} (K_{++} + K_{--}) c + O(c^{3/2}) \quad (28)$$

which was obtained from the theorem of the second virial coefficient due to Meeron and is numerically identical with the Meeron (Ref.17) result. The difference is only analytical; the above formulation has the advantage to make the so-called Bjerrum association constant K_A explicit. The δ and δ' functions will be found in the original publication (Ref.16). Eq.(28) constitutes an exact evaluation of the system of eqs.(3,4) up to the linear term included.

LINEAR RESPONSE IN TRANSPORT PROPERTIES: LOW FIELD CONDUCTANCE

On a theoretical point of view the problem of electrolytic conductance is still more complicated since the concentration dependance of the motion of the ions depends not only on the equilibrium distribution functions but in addition on the perturbation brought by the external electrical field to these distribution functions. Moreover, no simple equation as the compressibility equation (4) is available which might be used as a very practical starting point like it was done in the preceding section. However the derivation of a simple set of equations for conductance similar to eqs.(10,11) is highly desirable since it is rather straightforward to make precision measurements in the dilute concentration range where such a formulation is valid ($\kappa q \gamma^{1/2} < 0.5$).

In fact, such a system of equations was proposed and used with success formerly (Ref.18&19), but it needed the a priori assumption that the Bjerrum correction could be grafted on original conductance equations based on the Debye approximation, i.e. the linearization of the Poisson-Boltzmann equation. The result was

$$\begin{cases} \Lambda = \gamma \Lambda^L(R, c, \gamma) \\ \frac{1 - \gamma}{\gamma^2 c f_{\pm}^2} = K_A = \int_0^R 4\pi r^2 \exp\left(-\frac{U_{+-}}{kT}\right) dr \end{cases} \quad (29)$$

where the $\Lambda^L(R, c, \gamma)$ function is obtained by using former theoretical derivations $\Lambda(a, c)$

available and replacing simply \underline{a} by \underline{R} and \underline{c} by \underline{cY} . Note that eq.(29) proceeds from $\Lambda(a,c)$ functions just as eq.(10) proceeds from the original Debye-Hückel eq.(27).

However, in spite of the progress observed (Ref.19) by using the set of eqs.(29,11) this generalization met some opposition (Ref.20&21) which may be compared to that met originally by Bjerrum formulation. It was thus felt that it was necessary to proceed to a rederivation which would lead to a formulation of conductance analogue to eqs.(2-4,11).

This was made possible (Ref.22) by a reexamination of the basic equation of the Onsager treatment. Briefly summarized the main lines are the following. The most important point is the derivation of the perturbation to the distribution functions $g_{ij}^!$ as a consequence of the external perturber \underline{X} . Once these functions are known both the relaxation field $\Delta\underline{X}$ and the electrophoretic velocity Λ_{e1} which control the concentration dependence of the molar conductance can be obtained and the molar conductance is given by

$$\Lambda = \Lambda_0 \left(1 + \frac{\Delta X}{X} + \frac{\Lambda_{e1}}{\Lambda_0} \right) \quad (30)$$

where Λ_0 is the limiting value of the molar conductance which is an adjustable parameter. The basic equation for the derivation of $g_{ij}^!$ is the Onsager (Ref.3) continuity equation which merely states the mass conservation at the level of the two-particle reference space.

$$\nabla_P g_{jQ}^{iP} \vec{v}_{jQ}^{iP} + \nabla_Q g_{iP}^{jQ} \vec{v}_{iP}^{jQ} = 0 \quad (31)$$

where g_{jQ}^{iP} and \vec{v}_{jQ}^{iP} are the distribution function and the mean velocity vector of an ion of type i located at P when an ion of type j is present at Q .

One obvious property of any two-particle mean quantity is that it tends to the corresponding one-particle quantity when the restriction imposed during the averaging disappears (that is for \vec{v}_{jQ}^{iP} , for instance, when the location Q of the ion of type j goes to infinity with respect to P).

Consequently, the two particle mean velocity vector can be written as

$$\vec{v}_{jQ}^{iP} = \vec{v}^{iP} + \vec{w}_{jQ}^{iP} \quad (32)$$

where \vec{v}^{iP} is the mean velocity vector of an ion of type i at P (without any restriction for the averaging) and \vec{w}_{jQ}^{iP} is the correction which has to be brought for the presence of an ion of type j at Q . Of course, the excess vector \vec{w}_{jQ}^{iP} goes to $\vec{0}$ as Q goes to infinity. When eq.(32) is introduced in eq.(31) one important result is reached: it states that the perturbation on the pair distribution function of the form

$$g_{ji}^!(\vec{r}) = y_{ji}(r) \cos \frac{(\vec{v}^i - \vec{v}^j) \cdot \nabla_x}{kT(\omega_i + \omega_j)} \quad (33)$$

where \vec{v}^i and \vec{v}^j are new notations for \vec{v}^{iP} and \vec{v}^{jQ} which do not depend on location in the case of homogeneous solutions; ∇_x is the unit vector in the direction of external field \underline{X} ; ω_i^{-1} and ω_j^{-1} are the friction coefficients of the ions in the pure solvent which are directly related to the limiting conductances; \vec{r} is the vector \vec{PQ} and θ is the angle between the vectors \vec{PQ} and \underline{X} . Eq.(33) tells us that there is no perturbation for the distribution functions of ions of same type, a wellknown result. It also shows that the real cause of the perturbation of ion-pair distribution functions is not so much the external field itself but rather the fact that ions do not move identically under the excitation of the external field as is the case when $\vec{v}^i = \vec{v}^j = \vec{0}$. In the case of a binary symmetrical electrolyte eq.(33) can be rewritten as

$$g_{ji}^!(\vec{r}) = y_{ji}(r) \cos \frac{e_i X}{kT} \frac{\Lambda}{\Lambda_0}, \quad (34)$$

so that one sees that the theory of the conductance coefficient Λ/Λ_0 depends on $g_{ji}^!(\vec{r})$ as explained above but that $g_{ji}^!(\vec{r})$ in turn depends on Λ/Λ_0 . This important result was called the "echo effect" by one (Ref.22) of the authors and is at the basis of the Bjerrum type reformulation of the conductance equation which we are looking for.

So far in the available theoretical derivations found in the literature, the factor Λ/Λ_0 in eq.(34) is always missing, so that all evaluations of the functions $g_{ji}^!$ are incorrect as well the evaluation of the relaxation and electrophoretic terms $\Delta x/x$ and Λ_{e1}/Λ_0 , which shall be then denoted by $g_I^!$, $\Delta X_I/X$ and Λ_{e1I}/Λ_0 .

The corrections necessary to obtain the correct values are straightforward and read

$$g_{ji}^! = g_{jiI}^! \left(1 + \frac{\Delta X}{X} + \frac{\Lambda_{e1I}}{\Lambda_0} \right) \quad (35)$$

$$\frac{\Delta X}{X} = \frac{\Delta X_I}{X} \left(1 + \frac{\Delta X}{X} + \frac{\wedge e1}{\wedge_o} \right) \quad (36)$$

$$\frac{\wedge e1}{\wedge_o} = \frac{\wedge e1I}{\wedge_o} \left(1 + \frac{\Delta X}{X} + \frac{\wedge e1}{\wedge_o} \right) \quad (37)$$

The case of the electrophoretic velocity summarized by eq.(35) is more complicated and necessary details are to be found in the original publication (Ref.22).

The relaxation field contains a hydrodynamic contribution $\Delta X_h/X$ and a non hydrodynamic one $\Delta X_C/X$. Since each relaxation field term is a space integral over the direct ion-ion interaction weighted by the corresponding ion-pair distribution function, it can be parted into short-range and long-range contributions just like the G_{ij} functions in eqs.(5,6). Let us denote $\Delta X_C^S/X$ and $\Delta X_C^L/X$ the two contributions obtained from the non hydrodynamic contribution. It comes

$$\frac{\Delta X}{X} = \frac{\Delta X_C^S}{X} + \frac{\Delta X_C^L}{X} + \frac{\Delta X_h}{X} \quad (38)$$

Of course the echo effect applies to $\Delta X_C^S/X$ which can be written also as

$$\frac{\Delta X_C^S}{X} = \frac{\Delta X_{CI}^S}{X} \left(1 + \frac{\Delta X}{X} + \frac{\wedge e1}{\wedge_o} \right) \quad (39)$$

Substitution of eq.(39) in eq.(38) and of the result in eq.(30) leads straightforwardly to the following result

$$\left\{ \begin{array}{l} \wedge = \gamma \wedge_o \left(1 + \frac{\Delta X_C^L}{X} + \frac{\Delta X_h}{X} + \frac{\wedge e1}{\wedge_o} \right) \\ \frac{1-\gamma}{\gamma} = - \frac{\Delta X_{CI}^S}{X} \end{array} \right. \quad (40)$$

$$\quad (41)$$

where γ is an intermediary variable defined by

$$\gamma = \frac{1}{1 - \frac{\Delta X_{CI}^S}{X}} \quad (42)$$

The analogy between eqs.(40,42) and the equilibrium results given by eqs.(3,4,7) is obvious. It is wellknown that the relaxation effect $\Delta X_{CI}^S/X$ is on the overall a braking effect since it tends to decrease the velocity of the ions. Consequently $\Delta X_{CI}^S/X$ is negative so that γ here is a dimensionless number which follows the inequalities given by eq.(8). The identity between eq.(7) and eq.(42) was proved by Justice and Ebeling (Ref.23) using for the evaluation of the short range contribution $\Delta X_{CI}^S/X$ the so-called strong coupling approximation which transpires from the results obtained at equilibrium. This approximation states that, when the direct interaction between two ions of opposite charge is large then only their pair distribution function g_{iP}^{jQ} is perturbed, not their relative two particle velocity \vec{v}_{iP}^{jQ} so that

$$\vec{v}_{iP}^{jQ} - \vec{v}_{jQ}^{iP} = \vec{0} \quad \text{for } r < R \quad (43)$$

Using eq.(43) in the short range region instead of the Onsager equation (31) leads to

$$\frac{\Delta X_{CI}^S}{X} = -c G_{+-}^S + O(c^{3/2}) \quad (44)$$

where the $O(c^{3/2})$ contribution is numerically quite small compared to the G_{+-}^S contribution. The immediate consequence is the following result for conductance

$$\wedge = \gamma \wedge^L(R, c\gamma) + O(c^{3/2}) \quad (45)$$

$$\frac{1-\gamma}{\gamma c^{\frac{1}{2}} \wedge^L} = K_A = \int_0^R 4\pi r^2 \exp\left(-\frac{U_{+-}}{kT}\right) dr \quad (46)$$

This gives the evidence that excess conductance and excess equilibrium thermodynamic data lead to the same information as far as the direct energy of interaction U_{+-} is concerned.

EXPERIMENTAL VERIFICATION AND RESULTS

Before proceeding to a systematic analysis of conductance data it is necessary to make, whenever possible, a test in order to check that both experimental methods (thermodynamics and conductance) can in fact be reduced in terms of parameters having the same information content as can be expected from the above review.

One way to do so is to evaluate from conductance data the apparent distance of closest approach a' and from this parameter to obtain a calculated value of the activity coefficient which can then be compared with corresponding observed values. For the few aqueous systems where this is possible (i.e. for which there exist such thermodynamic data in the adequate concentration range) the results found (Ref.24) were satisfactory. They concern mainly alkali salts with monovalent oxoanions. When the thermodynamic data do not exist in low enough concentrations another method must be used which consists in comparing directly the reduced parameters. A convincing example of such procedure will be presented here.

Recently Pitzer et al. (Ref.25) have started with a thorough reanalysis of excess thermodynamic data up to rather high concentrations. They used the following relation:

$$\phi - 1 = -\frac{1}{3} \frac{\kappa q}{c^{1/2}} d_o^{1/2} \frac{m^{1/2}}{1+1.2m^{1/2}} + m (\beta^{(0)} + \beta^{(1)} e^{-2m^{1/2}}) + m^2 c \phi \quad (46)$$

in which ϕ is the osmotic coefficient, d_o the density of the solvent and m the molality; $\kappa q/c^{1/2}$ is the Debye-Hückel limiting law coefficient; $\beta^{(0)}$, $\beta^{(1)}$ and $c\phi$ are the three adjustable parameters which were found sufficient to reduce the original data up to $c = 3M$ sometimes. Eq.(46) derived by Pitzer is a semi-empirical formula which basically can be obtained by utilizing the Debye-Hückel distribution function in the Rasaiah-Friedman pressure equation (Ref.7).

The Pitzer equation (46) after conversion of molality m into molarity c and expansion can be rewritten as

$$\phi - 1 = -\frac{1}{3} \frac{\kappa q}{c^{1/2}} c^{1/2} + \left[\frac{1.2}{3} \frac{\kappa q}{c^{1/2}} + \beta^{(0)} + \beta^{(1)} e^{-2c^{1/2}} \right] c + O(c^2) \quad (47)$$

which can now be compared to

$$\begin{aligned} \phi - 1 = & -\frac{1}{3} \frac{\kappa q}{c^{1/2}} c^{1/2} + \frac{1}{2} \kappa q R \left[1 - \delta \left(\frac{q}{R} \right) + \delta' \left(\frac{q}{R} \right) \right] - \frac{1}{2} c K_A e^{-2\kappa q} - \frac{1}{4} c \left[K_{++} + K_{--} \right] e^2 + \\ & + O(c^{3/2}) \end{aligned} \quad (48)$$

which is the transform of eq.(28) through the use of the Gibbs-Duhem equation [cf. eq.(37) in Ref.16]

Neglecting the K_{++} and K_{--} contributions which can be but very small due to the high electrostatic repulsion between ions of same signs in the short range region; noting that in water $\kappa q/c^{1/2} = 1.178$ and that for $R=q$, $\delta(q/R) = 1/3$ and $\delta'(q/R) = 1/6$, the following identity is found

$$K_A \equiv -2(\beta^{(0)} + \beta^{(1)} - 0.10) \quad (49)$$

between eq.(47) and eq.(48). The idea is then to compare the evaluation of K_A from conductance with the parameters $\beta^{(0)}$ and $\beta^{(1)}$ evaluated by Pitzer.

In fact, due to the semiempirical aspect of eq.(47) and to the very different range of concentration used in both techniques, systematic deviations are to be expected which hopefully can be eliminated by introducing in eq.(49) an arbitrary constant which will be determined by imposing the identity for KCl in water. This is convenient since conductance gives $K_A=0$ for this system. It comes, as a substitute to eq.(49) the following equation

$$K_A^* = -2 (\beta^{(0)} + \beta^{(1)} - 0.26) \quad (50)$$

where K_A^* now denotes the "association" constant calculated from Pitzer tables.

Table 1 summarizes the numerical comparison obtained.

TABLE 1. A comparison of association constants (K_A^*) calculated by eq.(50) from Pitzer's coefficients (Ref.25) $\beta^{(0)}$ and $\beta^{(1)}$ with those (K_A) evaluated from conductance measurements using the Fernandez-Prini (Ref.26) version of the Fuoss-Hsia (Ref.27) equation.

Sel _{MX}	$\beta^{(0)}$	$\beta^{(1)}$	K_A^*	K_A	ref.
RbCl	0.044	0.148	0.14	0.18	a
CsCl	0.030	0.056	0.35	0.37	b
RbBr	0.040	0.153	0.13	0.11	c
CsBr	0.028	0.014	0.44	0.39	d
RbI	0.040	0.133	0.17	0.04	e
CsI	0.024	0.026	0.42	0.28	d
NaNO ₃	0.007	0.178	0.15	0.21	f
K NO ₃	-0.082	0.049	0.59	0.73	f
RbNO ₃	-0.079	-0.017	0.71	0.82	f
CsNO ₃	-0.076	-0.067	0.80	1.00	f
NaBrO ₃	-0.021	0.191	0.18	0.21	f
K BrO ₃	-0.129	0.257	0.26	0.53	f
K ClO ₃	-0.096	0.248	0.21	0.59	g
Me ₄ NBr	-0.036	-0.201	1.00	1.15	h,j
Et ₄ NBr	-0.046	-0.448	1.50	1.1	i,j
Pr ₄ NBr	0.011	-0.826	2.15	1.1	i,j
Bu ₄ NBr	-0.056	-0.579	1.79	0.96	i,j
Me ₄ NI	0.035	-0.585	1.62	1.45	i,j
Et ₄ NI	-0.193	-0.599	2.10	2.47	i,j
Pr ₄ NI	-0.284	-0.863	2.80	2.81	i,j

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 c - J.-E.Lind,jr. and R.M.Fuoss, J.Phys.Chem., 66, 1727 (1962)
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 h - M.Quintin and M.-C.Justice, C.R.Acad.Sci.Paris, 261, 1287 (1965)
 i - M.-C.Justice and J.-C.Justice, C.R.Acad.Sci.Paris, 262, 608 (1966)
 j - D.F.Evans and R.L.Kay, J.Phys.Chem., 70, 366 (1966)

Again one observes a very good agreement which underlines the internal consistency of both data reducing techniques.

Another verification consists in comparing the conductance results with those of Rasaiah and Friedman (Refs.10&11) relative to the square potential of the anion-cation Gurney cosphere overlap obtained from HCN treatment of osmotic coefficient data. This model is defined by the following relations:

$$U_{ij}(r)/kT = \begin{cases} \infty & \text{for } r < r^+ + r^- = a_{ij} \\ d_{ij}/kT + z_i z_j \frac{2q}{r} & \text{for } a_{ij} < r < a_{ij} + d \\ z_i z_j \frac{2q}{r} & \text{for } r > a_{ij} + d \end{cases} \quad (51)$$

where z_i and z_j are the algebraic charge numbers of the ions, $d=2.76$ the diameter of a water molecule and r^+ and r^- are the Pauling radii of the ions. This verification implies the reduction of conductance data in term of the same parameter d_{+-}/kT . This is readily achieved by a least square adjustment of the apparent distance of closest approach a' from conductance data and by use of the equivalent model theorem which states that, in dilute solutions, all hamiltonian models $U_{+-}(r)$ which lead to the same value for K_A in eq.(11) are equivalent, i.e. lead to the same observations as far as the non hydrodynamic part of the relaxation field $\Delta X_c/X$ of the conductance coefficient is concerned. The equation of correspondance is

$$\int_{a'}^R r^2 \exp\left(\frac{2q}{r}\right) dr = \int_0^R r^2 \exp\left(-\frac{U_{+-}^*}{kT} + \frac{2q}{r}\right) dr \quad (52)$$

where the left hand side represents the primitive model case characterized by a' and the right hand side any other equivalent model characterized by U_{+-}^* . It follows that once the

apparent distance a' is evaluated the corresponding value of the Rasaiah-Friedman d_{+-}/kT parameter is obtained through

$$\exp(-d_{+-}/kT) = \frac{\int_a^{a+d} r^2 \exp\left(\frac{2q}{r}\right) dr}{\int_{a'}^{a'+d} r^2 \exp\left(\frac{2q}{r}\right) dr}$$

Details on the adjustment of a' from conductance data will be found elsewhere (Ref.29). For the few cases where the comparison is possible, that is for most alkali halides in water the test is again quite satisfying (Refs.28&29).

Another test of self-consistency must be mentioned here. It consists in the great similarity of results obtained by Ebeling et al. (cf.Ref.29, p.323) from both thermodynamic and conductimetric sources which check with ours. A substantial number of data, for 1-1 salts in hydroxylic solvents were thus studied. The results are summarized in figures 1 - 7 where the observed values for d_{+-}/kT are plotted as a function of the sum a of Pauling's radii r^+ and r^- .

For alkali salts in water one observes a significant correlation between the two quantities since the bigger the value of a the more negative the value d_{+-}/kT as shown in fig.1.

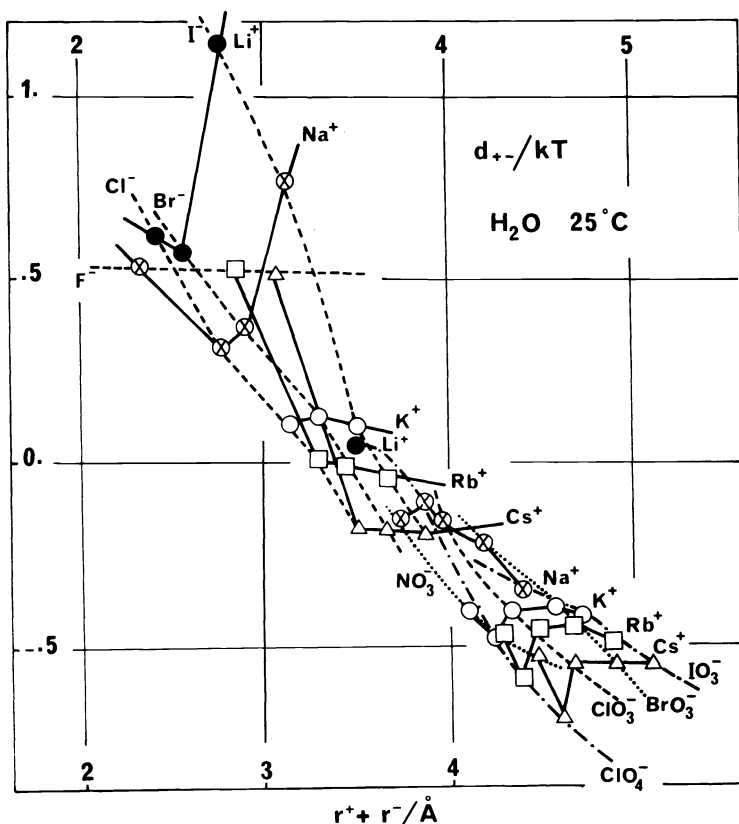


Fig. 1. Values of the specific Gurney-Friedman parameter d_{+-}/kT of the following model

$$U_{+-}/kT \begin{cases} \infty & \text{for } r < a \\ 2q/r + d_{+-}/kT & \text{for } a < r < a+d \\ 2q/r & \text{for } r > a+d \end{cases}$$

where $a=r^++r^-$ is the sum of the Pauling ionic radii, d is the diameter of the water molecule (2.76 Å), q the Bjerrum distance $e^2/2DkT$ and D the dielectric constant of the solvent. Full and dotted lines allow the identification of cations and anions respectively. References concerning the alkali-halides conductance data will be found in Ref.29. Chlorates and perchlorates data were taken from R.Bury, M.-C.Justice and J.-J.Justice, J.Chim.Phys., 67, 2045 (1970). Nitrates, bromates and iodates

data will be found in Ref.24.

This trend continues for tetraalkyl ammonium salts in water as seen on fig.2, since the corresponding points would just extrapolate on the bottom right part of Fig.1. However, for a given alkali cation the trend is not observed when the size of the anion increases whereas it is still observed for tetraalkylammonium ions. The case of these last salts is interesting since the same pattern is observed in alcohols as can be seen in figs.(2-4). Moreover, the longest is the alkyl chain of the alcohol the more negative becomes the d_{+-}/kT parameter.

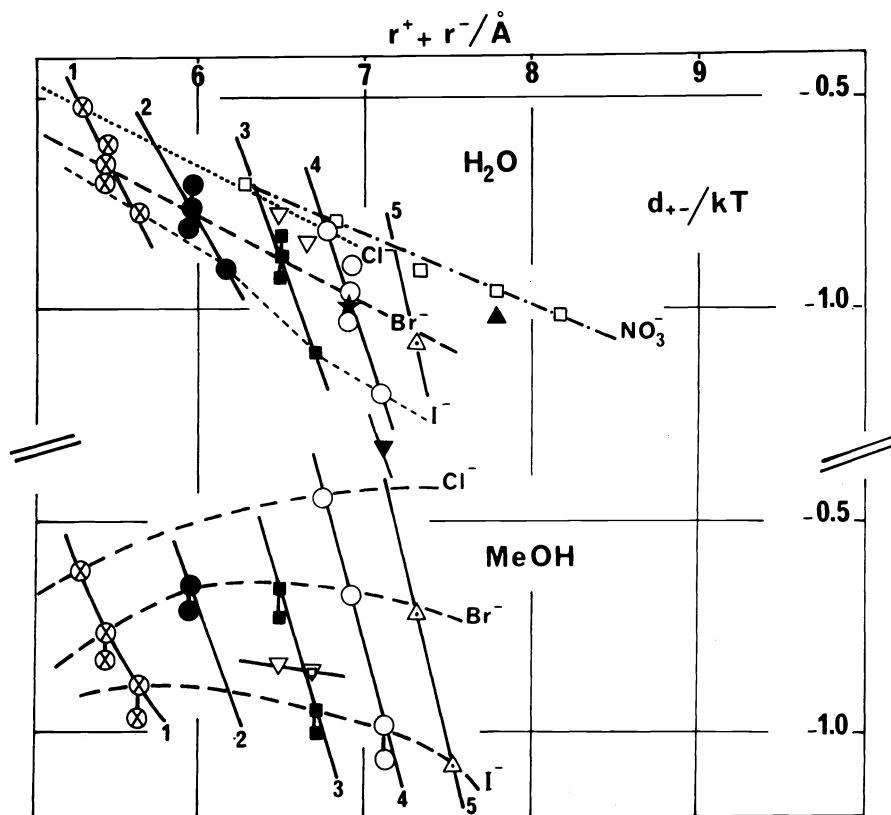


Fig. 2. Values of the parameter d_{+-}/kT for tetraalkylammonium salts in water and methanol. The successive full lines (1,2,...n...) identify the cations $[\text{CH}_3-(\text{CH}_2)_n]_4\text{N}^+$; the dotted lines indicate anions. In the case of the R_4NNO_3 salts \square in water, the length of the alkyl chain R increases by one $-\text{CH}_2-$ unit from left to right. The two ∇ points in H_2O and MeOH refer to $[\text{Et}(\text{OH})]_4\text{N}^+$ bromide and iodide from left to right; in MeOH the symbol ∇ refers to the iodide at 10°C and 25°C which both give the same results. When three points lie on the same vertical line, the lower refers to measurements at 10°C , the upper at 45°C ; when only two points lie on the same vertical line, the lower refers to measurements at 10°C , the higher at 25°C ; symbols \star , \blacktriangledown , \blacktriangle refer to triisooamylbutylammonium bromide, iodide and nitrate respectively. Except for the R_4NNO_3 salts in water which are data to be published by Y.Prigent, M.-C.Justice and J.-C.Justice, all other references will be found in Ref.29.

Also worth mentioning is the fact that d_{+-}/kT are more negative for 2-propanol than for both ethanol and n-propanol. Decreasing temperature also tends to give more negative d_{+-}/kT values. Changing Pr_4N^+ to $(\text{EtOH})_4\text{N}^+$ has not such a drastic effect as one might expect as can be seen by inspections of the ∇ points in fig.2.

On figures 5 and 6 one sees that changing the hydrogens of the alkyl ends of alcohols for fluorine keeps the pattern practically unchanged but lifts the values for d_{+-}/kT up to positive values.

Fig.7 clearly shows that changing the alcohol radical for the ketone one increases also the d_{+-}/kT values though much less but changes the pattern radically as shown by the reverse trend observed on the effect of anions. Clearly both the nature of alkyl chains and the hydrogen bonding character of the solvent play different and significant roles. This is one of the positive aspects of the present data reduction, to visualize with some details and to evaluate quantitatively these effects. It seems that we can thus reach valuable data whose interest is not only to enable one to recalculate excess thermodynamic quantities when those

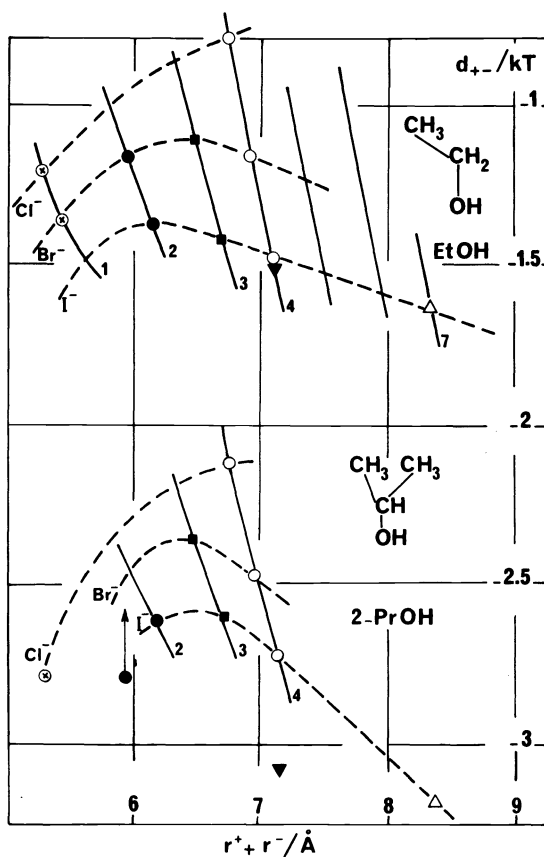


Fig. 3. cf. caption to fig. 2

Δ refers to tetraheptylammonium iodide conductance data by D.F. Evans and P. Gardam J. Phys. Chem. 72, 3281 (1968)

are not directly available but still more important to serve as basic quantities for the research of future theoreticians. However this last problem will be a difficult one since understanding these reduced excess parameters will prove as difficult as understanding the transfer quantities, both belonging to the field of dense particle systems. It is hoped, that the derivation of extensive sets of such data will help to develop new ideas of qualitative nature which in turn will be amenable to quantitative studies.

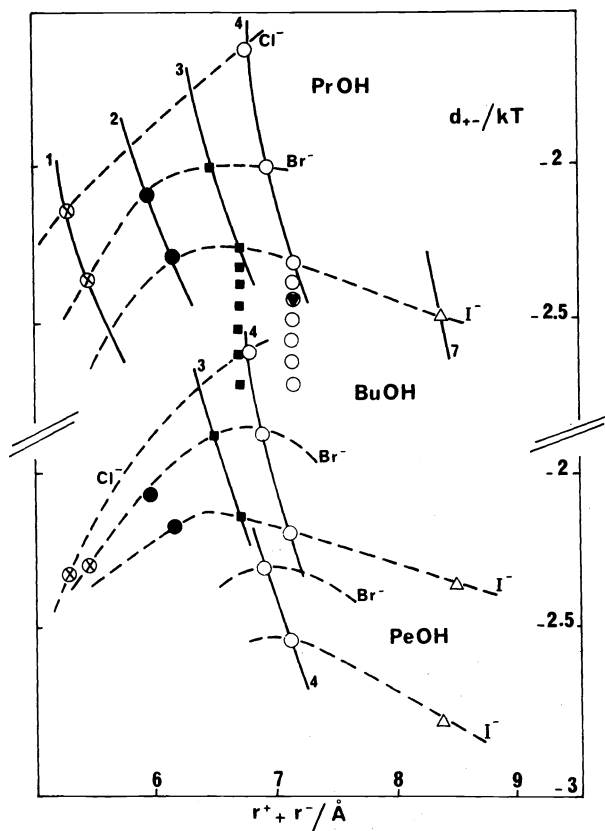


Fig. 4. cf. caption to fig.3

The vertical sequence of \blacksquare and \circ symbols refer to measurements from -40°C to 10°C by steps of 10° and 25°C , from bottom to top respectively, by R.Wachter, Dissertation, Univ.of Regensburg 1973. The arrow on the point relative to Pr_4NBr in 2-PrOH indicates the only point which does not fit in the general pattern. This is very probably due to an experimental error. Reference for original data are given in Ref.29.

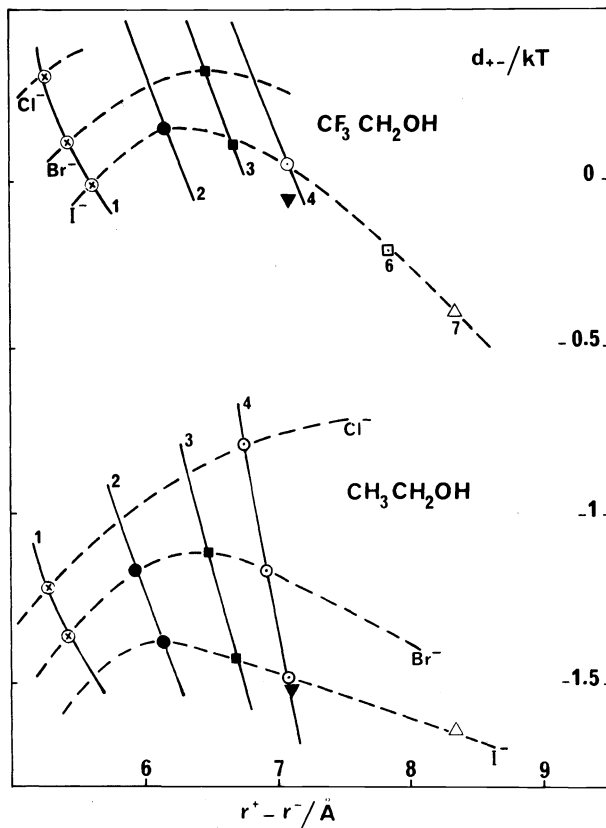


Fig. 5. Effect observed when changing from $\text{CH}_3\text{CH}_2\text{OH}$ to $\text{CF}_3\text{CH}_2\text{OH}$ solvents on the $d_{+ \cdot} / kT$ values of R_4N^+ halides - Source of original conductance data for ethanol are given in Ref.29; for trifluoroethanol: D.F.Evans, J.A.Nadas and M.A.Matesich, J. Phys.Chem., 75, 1708 (1971)

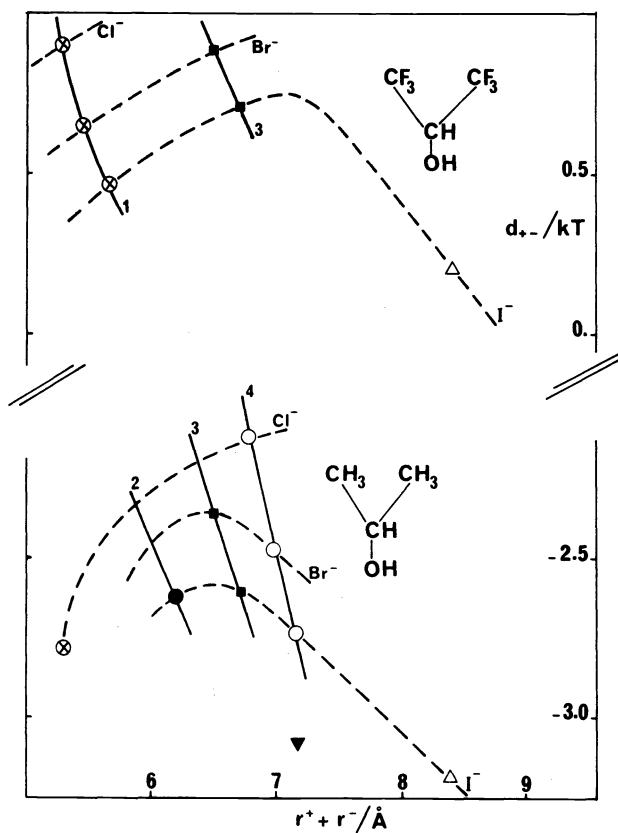


Fig. 6. Differences on d_{+-}/kT observed in hexafluoro-2-propanol and in 2-propanol. cf. Ref.29 for data source in 2-PrOH; In hexafluoro-2-propanol data were taken from M.A.Matesich, J.Knoefel, H.Felman and D.F.Evans, J.Phys.Chem., 77, 366 (1973).

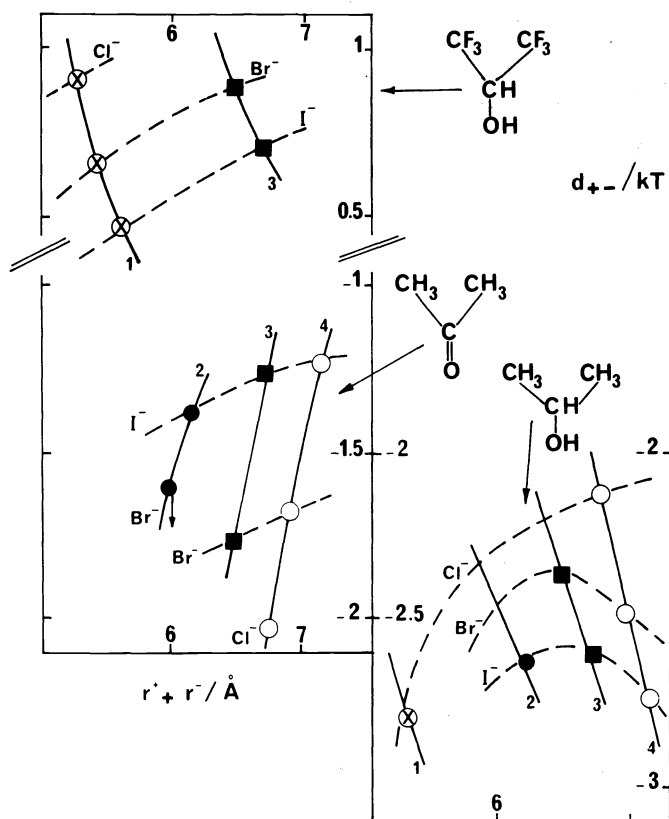


Fig. 7. Comparison of the d_{+-}/kT behaviour of R_4N^+ salts in three similar solvents concerning their molecular structure. Data source given in caption to fig.6. Original conductance data for acetone were taken from D.F.Evans, J.A.Nadas, J.Thomas and M.A.Matesich, *J.Phys.Chem.* 75, 1714 (1971).

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